DFT insights into the formation of sulfur vacancies over corner/edge site of Co/Ni-promoted MoS_2 and WS_2 under the hydrodesulfurization conditions

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ABSTRACT

The formations of sulfur vacancies over different active sites of Mo-based and W-based active phases are investigated under the traditional hydrodesulfurization (HDS) reaction conditions using DFT calculations. It can be found that under the HDS reaction conditions ($600\,K$, $p(H_2) = 4\,MPa$ and $p(H_2S)/p(H_2) = 0.001$), the single sulfur vacancy can be easily formed at the S-edge rather than the M-edge/W-edge. Comparably, with the promotions of Co or Ni atoms occurring at the S-edge of the MoS_2/WS_2 active phase, the formation of single sulfur vacancy will become more favorable at this site. Moreover, it is interesting that when Ni atoms further replace Mo atoms at the S-edge of NiMoS active phases, the formations of double sulfur vacancies become more favorable, which can expose more accessible Ni sites for the adsorptions of sulfur-containing compounds. And temperature and pressure are two important factors affecting the sulfur vacancy formation.

1. Introduction

As the environmental legislation becomes more and more strict, the refiners have to produce transportation fuels with ultra low sulfur levels in order to limit the emission of harmful sulfur-containing exhaust emissions into the atmosphere [1]. Currently, the catalytic hydrodesulfurization (HDS) reaction is still the main process used to remove sulfur-containing compounds from oil feedstock in the industry. Therefore, an atomiC–Scale understanding of the nature of the active sites will be greatly important to realize high efficiency for both the unpromoted and promoted Mo-based and W-based HDS catalysts. Especially, the insight into the site involved in the direct desulfurization (DDS) reaction is more desirable, since the conversions of the highly refractory organic sulfides such as dibenzothiophene (DBT) depend strongly on these active sites [2–4]. Recently, the information regarding the surface binding sites in Mo-based catalysts has been progressed greatly by the use of extended X-ray adsorption fine structure (EXAFS) spectroscopy technique, scanning tunneling microscopy (STM) together with more reliable density functional theory (DFT) calculations [5–13].

Based on the previous researches, it is widely recognized that the catalytic active sites in the HDS processes located on the "M-edge" and "S-edge" of the unpromoted MoS_2 or promoted MoS_2 [14–16]. According to the researches by Cristol et al. [17,18], the coordinatively unsaturated sites (CUS) or so-called sulfur vacancies created in a

reaction with hydrogen which stripped off one or more sulfur atoms from MoS_2 edges had high affinities for bonding with the sulfur-containing compounds, thus facilitating the removal of sulfur atoms. Moses et al. [19] reported that, the HDS processes could proceed at the M-edge without the creation of sulfur vacancies. However, at the S-edge, sulfur vacancies were necessary for the HDS reaction. In another research [20], Moses et al. found that the Co-promoted S-edge was "born with sulfur vacancies", meaning that sulfur vacancies were generated due to the changes of the metallic coordination number by Co promoter. Therefore, HDS reactions could occur at these sites without the removal of sulfur atom by hydrogen to create the corresponding sites for the adsorption of the probing molecule. Recently, Rangarajan and his coworkers [21–23] reported that unhindered sulfur-containing compounds, including H_2S, thiophene, and DBT could adsorb over the sulfur vacancies more strongly and undergo HDS reactions via the DDS pathway. Moreover, the sulfur vacancies located at the S-edge or corner sites were considered to contribute the maximum HDS activity.

Combed with the previous STM and DFT researches, it was reported that the vacancies could be generated at the corner sites as well as the edges [24–26]. Correspondingly, the sulfur vacancies located at the corners were also received extensive attentions. Šarić et al. [23] reported that DBT could adsorb planarly as well as perpendicularly over the corner vacancy, which could play an important role in the desulfurization of DBT molecule. Based on the researches by Grønborg
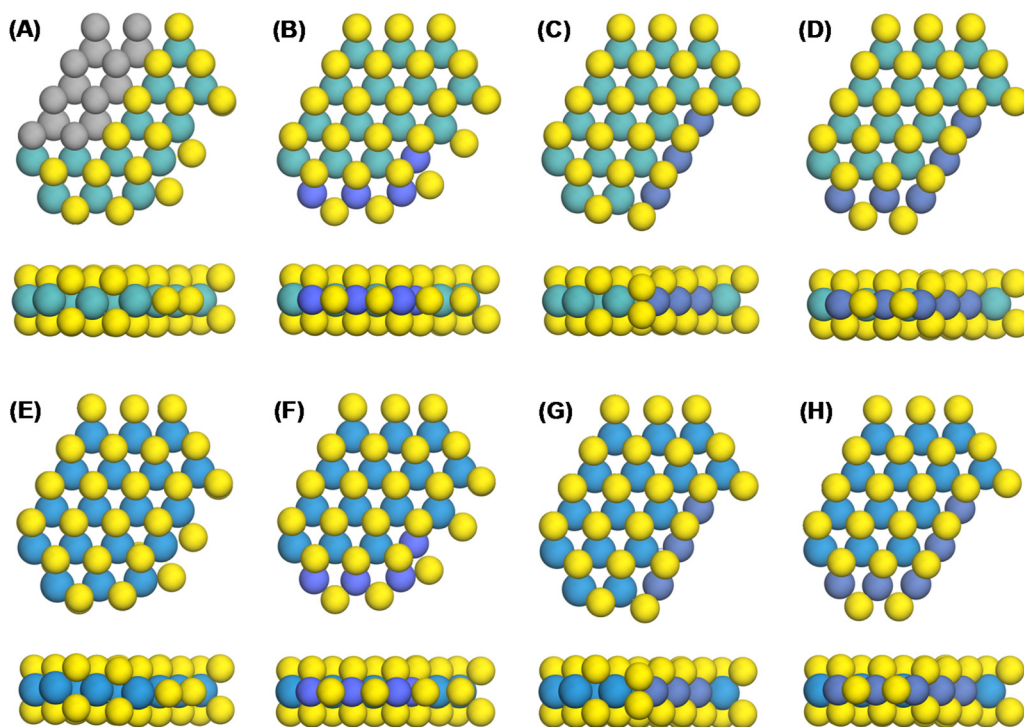

Fig. 1. Models of different corners: (A) MoS_2; (B) CoMoS; (C) NiMoS-I; (D) NiMoS-II; (E) WS_2; (F) CoWS; (G) NiWS-I; (H) NiWS-II, the light purple, dark purple, blue-green, blue and yellow spheres represented Co, Ni, Mo, W and S atoms, respectively. The light grey atoms were fixed at the positions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

et al. [25], the only possibility for direct chemisorption of 4,6-DMDBT on the Co-promoted MoS_2 was through the sulfur vacancy in the corner site. And the DFT calculations exhibited that the formation of sulfur vacancy over the corner sites of the S-edge was relatively difficult under the HDS conditions. However, according to Rangarajan et al.'s researches [21], the adsorption of N-containing compounds was stronger than that of S-containing compounds over all active sites except the corner site or the sulfur edges of CoMoS active phases, which were proposed as required for minimum inhibition. Therefore, it could be found that the possible formation positions of the sulfur vacancies were needed, which were considered to be more important in the analysis of the adsorption sites of the macromolecule S-compounds, such as DBT and 4,6-DMDBT. Although some considerable theoretical and experimental researches have been devoted to investigating the active sites over the unpromoted or promoted MoS_2, a deep insight into the structure of the active sites at the surfaces of WS_2 is still needed [27,28].

Therefore, DFT calculations were performed to investigate the formations of sulfur vacancies over different sites of Mo-based and W-based catalyst surfaces with the thermal and entropic corrections in this research. Particularly, the temperatures (550~650 K) and the pressures ($p(H_2) = 4$ MPa and $p(H_2S)/p(H_2) = 0.1$ and 0.001) which were close to HDS conditions were considered. Firstly, the formations of single or double sulfur vacancies over the MoS_2, NiMoS and CoMoS active phases were investigated. Secondly, the formations of the sulfur vacancies over the surfaces of W-based active phases were studied. Following those calculations, the comparisons between unpromoted and promoted MoS_2 active phases and the comparisons between W-based and Mo-based active phases were discussed systematically.

2. Computational details

2.1. Computational methods

The DFT calculations are performed through DMol^3 package with double-numeric polarized basis set [29,30]. The exchange-correlation energy is calculated within the generalized gradient approximation (GGA) using the function proposed by Perdew and Wang (PW91)

[31,32]. The Brillouin zone integrations are performed using $2 \times 2 \times 1$ k-points in the x, y and z directions, respectively. Structural optimizations are obtained on the basis of the convergence criterion in which SCF (Self Consistent Field) tolerance is 1.0×10^{-6} Ha, while the convergence tolerances of maximum force 1.0×10^{-3} Ha/Å. A Fermi smearing of 2.0×10^{-3} Ha and a cutoff radius of 4.5 Å are used to accelerate convergence. Spin states are explicitly set. Furthermore, all the vibrational frequencies are calculated from the Hessian matrix.

2.2. Computational models

CoMoS and NiMoS active phases have been studied by considerable spectroscopy, microscopy and DFT researches [10–14]. The typical characteristics are described as follows: (1) the active sites locate at or close to the edges (M-edge and S-edge) [11,12]; (2) Co and Ni atoms can substitute the edge Mo atoms partially or completely [14,23]; (3) the incorporation of Co or Ni atoms increase the formation of coordinatively unsaturated sites [10,22]. (4) Co atoms replace the Mo atoms at the S-edge preferentially while the Ni atoms prefer the M-edge [13,23]. Therefore, through the models proposed by Šarić et al. [24,25], the CoMoS model is constructed, in which the Co atoms are primarily located at the S-edge. Furthermore, two different NiMoS models are considered: NiMoS-I and NiMoS-II models. NiMoS-I model is built based on the pure MoS_2, where the Mo atoms of the M-edge are substituted by the Ni atoms preferentially. For a better comparison, NiMoS-II model is built based on the NiMoS-I model, where a further Ni-substitution at the S-edge is taken into the consideration. With the Mo atoms of the S-edge replaced by the Ni atoms, the sulfur coverage of S-edge becomes 50% over NiMoS-II active phase compared with 100% over NiMoS-I active phase. Fig. 1 is the front and vertical views of different active phases. As shown in Fig. 1, a stepped stripe is used, which is continuous in the x direction. And a 15 Å vacuum is considered to make sure the slab is isolated in the y-direction and z-direction. The grey atoms are fixed at the positions. Fig. 1(A) is the initial model of MoS_2 active phase, in which the sulfur coverage of S-edge is 100% and the sulfur coverage of M-edge is 50%. Fig. 1(B) is the initial model of CoMoS active phase, in which the sulfur coverage of S-edge is 50% due to the promotion effect of Co atoms and the sulfur coverage of M-edge is
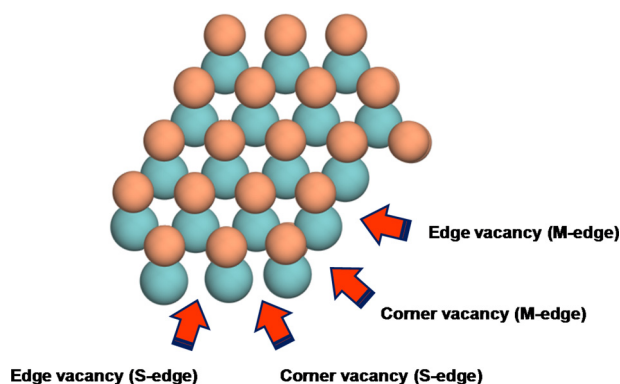
Fig. 2. Diagrammatic sketch of sulfur vacancies at different sites over transition metal sulfides, the orange and light green balls represent sulfur and Mo(W) atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

also 50%. Fig. 1(C) is the initial model of NiMoS-I active phase, in which the sulfur coverage of S-edge is 100% and the sulfur coverage of M-edge is 0. Fig. 1(D) is the initial model of NiMoS-II active phase, in which the sulfur coverage of S-edge is 50% and the sulfur coverage of M-edge is also 0, considering the promotion effect of Ni atoms. The descriptions of W-based active phases are the same as those of Mo-based active phases. Fig. 2 is the diagrammatic sketch of sulfur vacancies generated at different sites over Mo-based or W-based active phase.

2.3. Thermodynamic calculations

The Gibbs free energy variations are evaluated in order to take considerations of the thermal and the entropic contributions. Based on the previous researches [13,16,24,26], the ΔG can be calculated according to *Equation (1)*, and a detailed description for calculating the vacancy formation energies can be obtained in the ***Supporting Information***.

$$\Delta G = \Delta E_0 + \Delta H_{Total} - T\Delta S_{Total}^T + kT\ln\left(\frac{p_{H_2S}}{p^0}\right) - kT\ln\left(\frac{p_{H_2}}{p^0}\right) \quad (1)$$

where ΔE_0 is the energy change of the corresponding reaction calculated at 0 K, ΔH is the enthalpy change, and ΔS^T is the entropy change at standard pressure ($p^0 = 1.0$ atm). In addition, k is the ideal gas constant, p is the partial pressure of each gas component. In this research, the phase diagrams are drawn at 600 K. In the phase diagrams, 600 K, p(H$_2$) = 4.0 MPa and p(H$_2$S)/p(H$_2$) = 0.001 are denoted as the HDS condition 1, 600 K, p(H$_2$) = 4.0 MPa and p(H$_2$S)/p(H$_2$) = 0.1 are denoted as the HDS condition 2. Furthermore, the changes of ΔG with the temperature (550 K ~ 650 K) and related thermodynamics parameters are provided in Tables S1–S12.

3. Results and discussion

3.1. Sulfur vacancy formation over Mo-based active phases

3.1.1. MoS$_2$ active phases

Firstly, the formations of a single sulfur vacancy over the corner and edge sites of the unpromoted MoS$_2$ active phase are calculated. In Fig. 3, it can be seen that with the increase of the H$_2$S partial pressure, the HDS reaction condition will move right gradually in the phase diagram and eventually breaks away from the phase region of sulfur vacancy generation. Accordingly, the reaction will proceed in reverse direction when the amount of H$_2$S is greater than that at the chemical equilibrium. Then H$_2$S molecule will re-adsorb over the vacancy site, which influences the formation of the sulfur vacancy. In addition, it can

be seen from the phase diagram (Fig. 3) that the difficulty of sulfur vacancy formation (from easy to hard) follows the sequence: Corner vacancy (S-edge) < Edge vacancy (S-edge) < Corner vacancy (M-edge) < Edge vacancy (M-edge). It is concluded that the S-edge is more beneficial for the formation of the single sulfur vacancy than the M-edge of the MoS$_2$ active phase without Ni or Co promotion.

According to the results in Fig. 3, it can also be found that the formation of one sulfur vacancy at corner site can be facilitated at both HDS conditions (600 K, p(H$_2$) = 4 MPa, p(H$_2$S)/p(H$_2$) = 0.1 or 0.001), however, which are not conducive to the formation of the sulfur vacancy at M-edge. Moreover, the sulfur vacancy can be generated at the edge site (S-edge) under the HDS condition of p(H$_2$S)/p(H$_2$) = 0.001 (low H$_2$S partial pressure). Contrastively, only the sulfur vacancy at the corner site (S-edge) can be generated under the condition of p(H$_2$S)/p(H$_2$) = 0.1 (high H$_2$S partial pressure).

From Fig. 3, the HDS condition 2 is very close to the phase region of one Edge vacancy formation (S-edge). Therefore, the corresponding ΔG under different temperatures (550 K ~ 650 K) are calculated and listed in Table S1. It can be seen that the values of ΔG decrease obviously with the increase of temperatures. It can be concluded that temperature is one of the factors affecting the sulfur vacancy formation, which will be beneficial for the formation of the sulfur vacancy with the increase of temperature. At the same time, it can be calculated that when p(H$_2$) = 8 MPa the value of $\Delta\mu$(H$_2$) is equal to 0.23 eV, this reaction condition is located in the phase region of the sulfur vacancy formation at edge site (S-edge). It is also deduced that pressure is also one of the important factors affects the sulfur vacancy formation. With the increase of pressure it will be beneficial for the formation of sulfur vacancy.

Considering that the sulfur vacancy at the corner site (S-edge) is most easily to be generated, the formations of double sulfur vacancies are calculated as shown in Fig. S1, including double Corner vacancies and double Edge vacancies, respectively. On the basis of one Corner vacancy (S-edge), it is easier to further remove the other sulfur atom at the S-edge rather than the sulfur atom at the M-edge. However, it can be seen from the phase diagram that the HDS conditions 1 and 2 (Fig. S1) are not located in the phase region of the double sulfur vacancies formation. Therefore, it can be found that the formation of double sulfur vacancies is relatively difficult over the unpromoted MoS$_2$ active phase.

Subsequently, the formation of double sulfur vacancies at the M-edge is comparably investigated as shown in Fig. S2. It can be found difficult to remove the second sulfur atom from the adjacent Mo atom based on the existence of one Corner vacancy (M-edge) under the HDS conditions 1 and 2. Moreover, compared with the results in Fig. S1, the HDS condition 1 in Fig. S1 is closer to the phase region of double sulfur vacancies formation. Therefore, it is speculated that the formation of double sulfur vacancies at the S-edge can be achieved by further increasing reaction temperature and H$_2$ pressure or reducing H$_2$S partial pressure. However, it can be found that when p(H$_2$) = 8 MPa ($\Delta\mu$(H$_2$) = 0.23 eV), the reaction condition is still not in the phase region of the double sulfur vacancies formation (S-edge) in Fig. S2. Therefore, it can be summarized briefly that the formation of double sulfur vacancies over the unpromoted MoS$_2$ active phase will be very difficult.

3.1.2. NiMoS active phases

Based on the researches of the sulfur vacancy formation over MoS$_2$ active phases, the formation of sulfur vacancies over the active sites of Ni-promoted MoS$_2$ active phase will also be investigated. Firstly, the Mo atoms of the M-edge are substituted preliminarily by Ni atoms to generate NiMoS-I model. From Fig. S3 (A), it can be seen that the HDS conditions 1 and 2 are not in the phase region of one Corner vacancy (S-edge) formation, which is different from those over the MoS$_2$ active phase. However, the reaction condition 1 is very close to the phase region. Therefore, it can be calculated that when p(H$_2$S)/p(H$_2$) = 10^{-5}, the value of $\Delta\mu$(H$_2$S) is equal to -0.41 eV, and this condition is located in the phase region. Furthermore, based on the results in Table S3, ΔG is
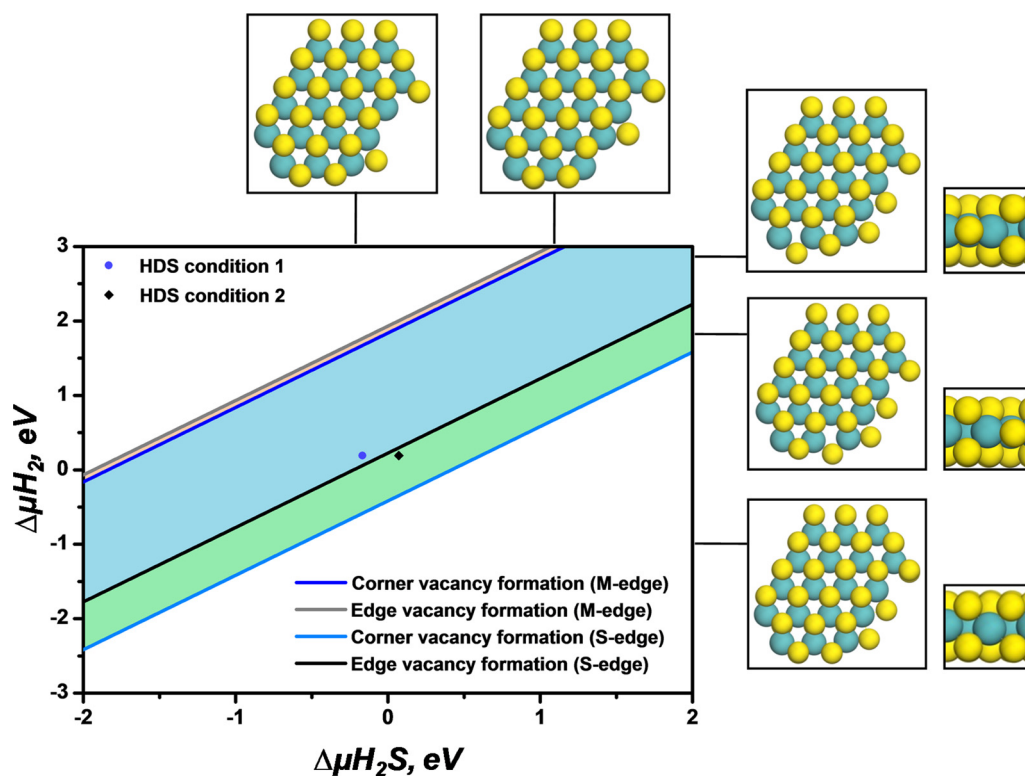
Fig. 3. Phase diagram for single sulfur vacancy formation over different sites of MoS$_2$ active phase (the HDS condition 1: T = 600 K, p(H$_2$) = 4 MPa and p(H$_2$S)/p(H$_2$) = 0.001; the HDS condition 2: T = 600 K, p(H$_2$) = 4 MPa and p(H$_2$S)/p(H$_2$) = 0.1).

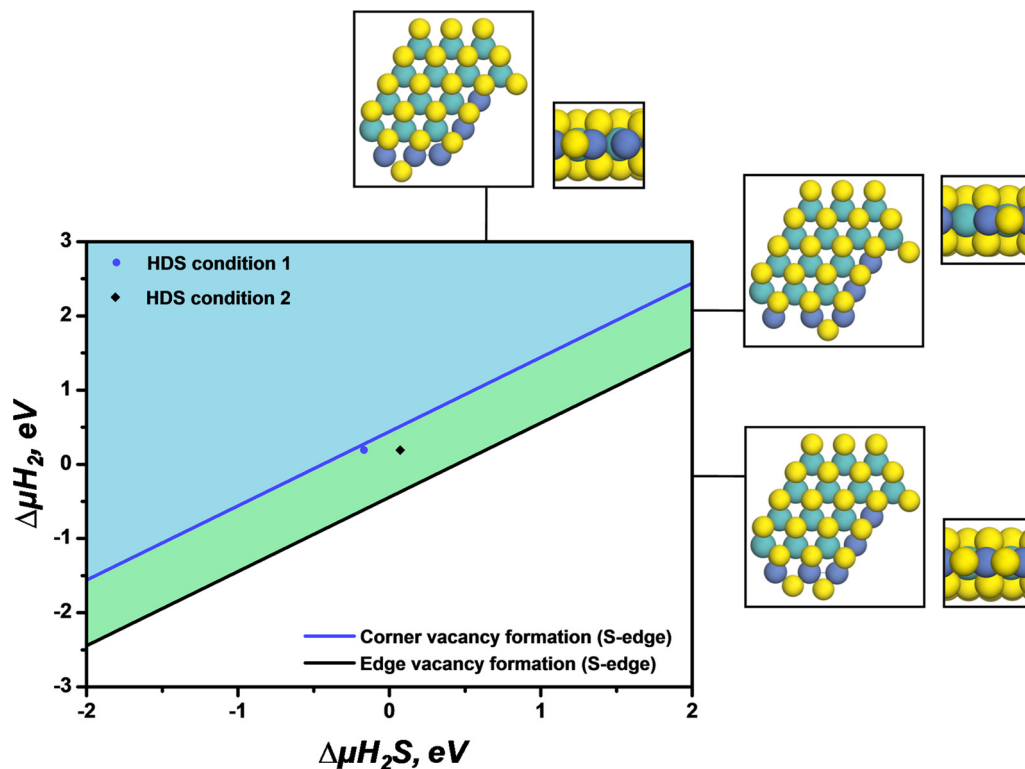**Fig. 4.** Phase diagram for single sulfur vacancy formation over the Corner or S-edge of NiMoS-II active phase.

great than 0 at p(H$_2$S)/p(H$_2$) = 0.001, while it is less than 0 at p(H$_2$S)/p(H$_2$) = 10^{-5}. Therefore, it can be deduced that the formation of a single sulfur vacancy is favorable at the corner site (S-edge) when the H$_2$S partial pressure is relatively low (at the initial stage of the reaction) over the NiMoS-I active phase. However, with the increase of H$_2$S partial pressure, the formation of such sulfur vacancy at the S-edge will become more difficult. More strict reaction conditions are needed to promote such sulfur vacancy formation.

Fig. S3 (B) is the phase diagram of a single sulfur vacancy formation over the S-edge of NiMoS-I active phase. From Fig. S3(B), the HDS conditions 1 and 2 are also not in the phase region. Compared with the results in Fig. S3(A), the HDS reaction condition 1 in Fig. S3(B) is farther from the phase region where sulfur vacancy can be generated, which means that the corner vacancy are more favored to be generated than the edge vacancy at the S-edge of NiMoS-I active phase. Therefore, compared with the formation tendency of a single sulfur vacancy over the unpromoted MoS$_2$ active phase, the difference is that the formation of the single sulfur vacancy at the S-edge becomes difficult when Ni atoms just occupy the M-edge. And the reaction temperature and pressure need to be further increased to form the corresponding sulfur vacancies.

In order to better compare with the formation mechanism of sulfur vacancies over MoS$_2$ active phase, the formation of double sulfur vacancies is also investigated as shown in Fig. S4. It can be seen that on the basis of one Corner vacancy (S-edge), the removal of another sulfur atom from the same Mo atom is more difficult to form the double sulfur vacancies. In addition, it can be also found that the HDS condition 1 is very close to the phase region. From Table S3, it can be seen that at p(H$_2$S)/p(H$_2$) = 10^{-5}, ΔG is less than 0, demonstrating that double sulfur vacancies are easier to be formed at very low H$_2$S partial pressure.

Subsequently, the Mo atoms of the S-edge are further replaced by Ni atoms to generate NiMoS-II model. And the formations of sulfur vacancies over the active sites of NiMoS-II active phase (S-edge is further occupied by Ni atoms) are also investigated as shown in Fig. 4. It can be found that the formation of a single sulfur vacancy at the edge site is more preferable than that at the corner site over NiMoS-II active phase, meaning that the sulfur vacancy at the edge site will be generated preferentially. Furthermore, compared with the formation of a single sulfur vacancy over the NiMoS-I active phase, it can be found that the HDS condition 1 and 2 are in the phase region of sulfur vacancy formation at the edge site of S-edge. Furthermore, when p(H$_2$S)/p(H$_2$) = 0.001, the HDS condition 1 is very close to the phase region of sulfur vacancy formation at the corner site of S-edge. Therefore, Table S4 provides the ΔG (550 K ~ 650 K) of one Corner vacancy (S-edge) formation over NiMoS-II active phase. It can be found that at T = 650 K and p(H$_2$S)/p(H$_2$) = 0.001, ΔG = 1.75 kJ/mol, while ΔG = −23.14 kJ/mol at T = 650 K and p(H$_2$S)/p(H$_2$) = 10^{-5} (Table S4). It is clear that ΔG becomes negative, meaning that further reducing the partial pressure of H$_2$S can promote the sulfur vacancy formation at the corner site over NiMoS-II active phase. Therefore, it can be concluded that with the Ni atoms occupying the S-edge of NiMoS active phase, the formation of single sulfur vacancy will become easier compared with that over the NiMoS-I active phase.

Considering that it is possible to generate one sulfur vacancy at the corner or edge site over the NiMoS-II active phase, the formation of double sulfur vacancies on the basis of these vacancies is further investigated as shown in Fig. 5. As can be seen from Fig. 5(A), double sulfur vacancies are difficult to be generated based on the existence of one Edge vacancy (S-edge). However, from Fig. 5(B) and Table S4, it can be clearly observed that double sulfur vacancies can be generated on the basis of one Corner vacancy (S-edge). Therefore, it can be inferred that at the initial stage of HDS reaction, there is a certain proportion of sulfur vacancies formed at the corner sites when the H$_2$S partial pressure is very low. On these basis, the second sulfur vacancy can be further generated, which is conducive to the adsorption of sulfur-containing compounds such as 4,6-DMDBT and is beneficial for the subsequent removal of sulfur atoms. Therefore, it can be concluded that when Ni atoms continue to replace Mo atoms at the S-edge of NiMoS active phase, the formations of double sulfur vacancies become more favorable.

3.1.3. CoMoS active phases

The formations of sulfur vacancies over different active sites of Co-promoted MoS$_2$ active phase are also studied in this research. Similarly, the formation of one single sulfur vacancy at the corner or edge site of CoMoS active phase is calculated. As can be seen from Fig. 6, it can be seen that the sulfur vacancy at the edge site of S-edge is also favorable to be generated. Compared with the NiMoS-II active phase (Fig. 4), it is found that the formation of one Corner vacancy (S-edge) is relatively difficult over the CoMoS active phase. From Fig. 6, it can be concluded that the difficulty of sulfur vacancy formation over the CoMoS active phase follows the order (from easy to hard): Corner vacancy (M-edge) < Edge vacancy (S-edge) < Edge vacancy (M-edge) < Corner vacancy (S-edge). Therefore, at the M-edge of CoMoS active phase the Corner vacancy is more favorable to be generated, while at the S-edge the Edge vacancy is more preferable to be formed.

And then, the phase diagrams of double sulfur vacancies are drawn based on the existence of a single sulfur vacancy at the M-edge as shown in Fig. S5. It can be found that the formation of double sulfur vacancies is easier at the M-edge rather than that at the corner site, meaning that it is much easier to remove another sulfur atom at the edge site of the M-edge rather than that at the corner site of the S-edge. In addition, it can be observed that the HDS reaction conditions 1 and 2 are not located in the phase region. Therefore, it can be proposed that the formation of double sulfur vacancies is relatively difficult for the CoMoS active phase compared with NiMoS active phase.

In addition, the formation of double sulfur vacancies at the S-edge (Fig. S6) is also calculated and compared with those located at the M-edge or Corner. From Fig. S6 (A), based on the existence of one Corner vacancy (S-edge), the formation of double sulfur vacancies can proceed under the HDS conditions 1 and 2. However, considering that it is difficult to generate one Corner vacancy (S-edge) over the CoMoS active phase (Fig. 6), the formation of double sulfur vacancies at the S-edge
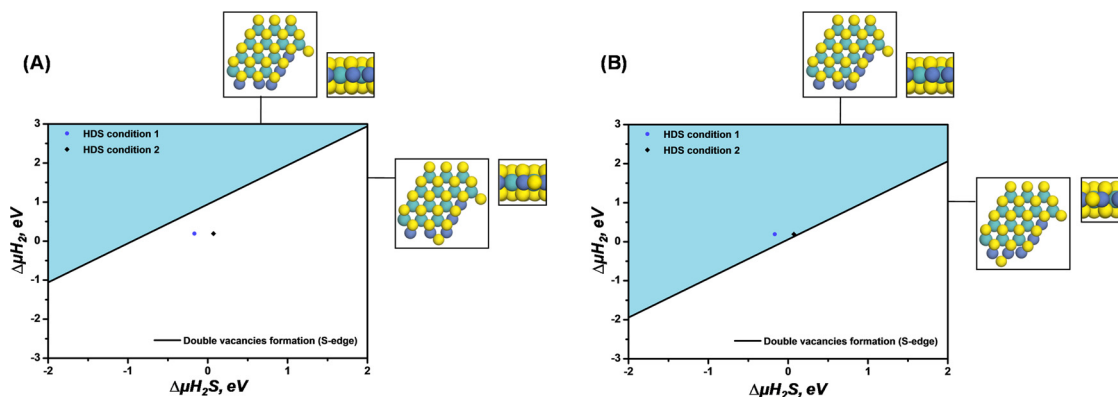

Fig. 5. Phase diagrams for double sulfur vacancies formation over the S-edge of NiMoS-II active phase: (A) from single vacancy at the S-edge; (B) from single vacancy at the Corner.
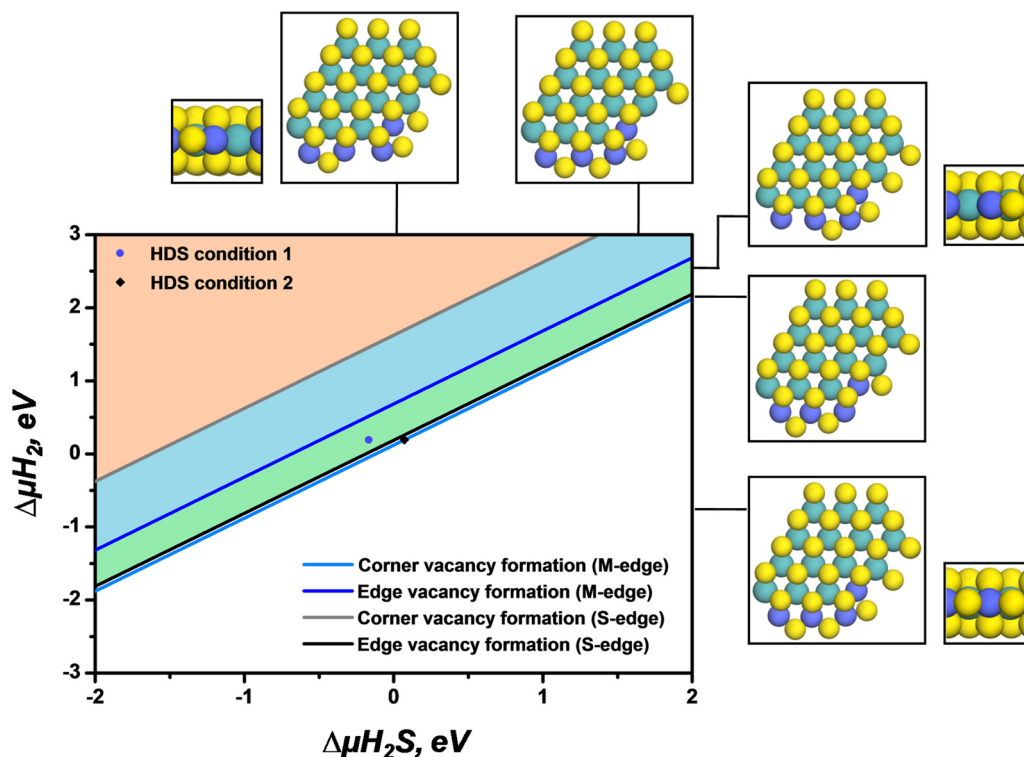
Fig. 6. Phase diagram for single sulfur vacancy formation over different sites of CoMoS active phase.

will be limited. In addition, based on the existence of one Edge vacancy (S-edge), the generation of double sulfur vacancies is also investigated in Fig. S6(B). It can be seen that the formation of the second vacancy cannot proceed spontaneously under HDS conditions 1 and 2, and both reaction conditions are far from the phase region. Table S6 provides the ΔG (550 K ~ 650 K) of double sulfur vacancies formation at the S-edge over CoMoS active phase. From the results in the table, it can be seen that all the values of ΔG are greater than 0 at 550 K ~ 650 K. Even by increasing reaction temperature and H_2 pressure or reducing H_2S partial pressure, it can be found that the formation of double sulfur vacancies is relatively difficult for CoMoS active phase. Combining the above calculation results, it can be inferred that the occurrence frequency of double sulfur vacancies will be very low near the corner site of the CoMoS active phase, which may further inhibit the chemical adsorption of sulfur-containing compounds such as 4,6-DMDBT, thus affect the direct desulfurization of such compounds.

3.2. Sulfur vacancy formation over W-based active phases

WS$_2$ is also widely used as the active metal phase of HDS catalyst in the industry, which possesses high hydrotreating activity. However, there are few DFT researches on this kind of active phase, besides the bulk phase properties of WS$_2$ reported in the series of theoretical studies about the transition metal sulfides by Raybaud et al. However, considerable studies have shown that NiWS active phase is also considered to play an important role in the HDS reaction. The DFT calculations on W-based active phases are similar to those of Mo-based active phases reported in the above sections. The formations of sulfur vacancies at the corner or edge site over the unpromoted and Ni(Co)-promoted WS$_2$ active phases are also studied. Therefore, the surface structures of W-based active phases can be explored from the micro-scale in order to fill the information gap in this field.

3.2.1. WS$_2$ active phases

Firstly, the formations of a single sulfur vacancy at different sites of WS$_2$ active phases are calculated. In Fig. 7, the HDS conditions 1 and 2

are the same as described in the above context. It can be seen that the difficulty of sulfur vacancy formation over the WS$_2$ active phase follows the order (from easy to hard): Edge vacancy (S-edge) < Corner vacancy (S-edge) < Corner vacancy (W-edge) < Edge vacancy (W-edge). Therefore, the S-edge of WS$_2$ is more conducive to the formation of a single sulfur vacancy than the W-edge, which is consistent with the results of MoS$_2$ active phase. However, one Edge vacancy (S-edge) of WS$_2$ is more favorable to be generated than the Corner vacancy (S-edge). In addition, according to the positions of HDS conditions 1 and 2 in Fig. 7, it can be seen that the formation of one Edge vacancy (S-edge) can be facilitated under both conditions of $p(H_2S)/p(H_2) = 0.1$ and $p(H_2S)/p(H_2) = 0.001$ (600 K), of which the HDS condition 1 is closer to the phase region of the Corner vacancy formation (S-edge). However, the formations of sulfur vacancies at the W-edge are also not seemed easily, which is corresponding to the results of MoS$_2$ active phases. Therefore, it is considered to be difficult for WS$_2$ active phase to generate a single sulfur vacancy at the W-edge under the traditional HDS conditions without the promotion of Ni or Co atoms.

Based on the existence of one Corner vacancy (S-edge), the formations of double sulfur vacancies at the corner and edge sites are investigated (Fig. S7). It can be seen that the double sulfur vacancies formed at the S-edge is easier, which is consistent with MoS$_2$ active phases. In addition, the HDS condition 1 is located in the phase region (Fig. S7), while the HDS condition 1 is not in the phase region over the MoS$_2$ active phase. Furthermore, for WS$_2$ active phase, the HDS condition 2 is very close to the phase region of double sulfur vacancies formation at the edge site (S-edge). Therefore, from Table S8, it can be found that the values of ΔG keep negative when $p(H_2S)/p(H_2) = 0.001$, meaning that the formation of double sulfur vacancies at the S-edge can occur at low H_2S partial pressure. Therefore, it can be seen that the S-edge of WS$_2$ active phase is more favorable for the generation of double sulfur vacancies compared with the S-edge of MoS$_2$ active phase. Subsequently, the formation of double sulfur vacancies at the W-edge is investigated as shown in Fig. S8. It can be seen that it is difficult to form double sulfur vacancies at the W-edge at both high and low H_2S partial pressures. Compared with the formation of double sulfur vacancies at
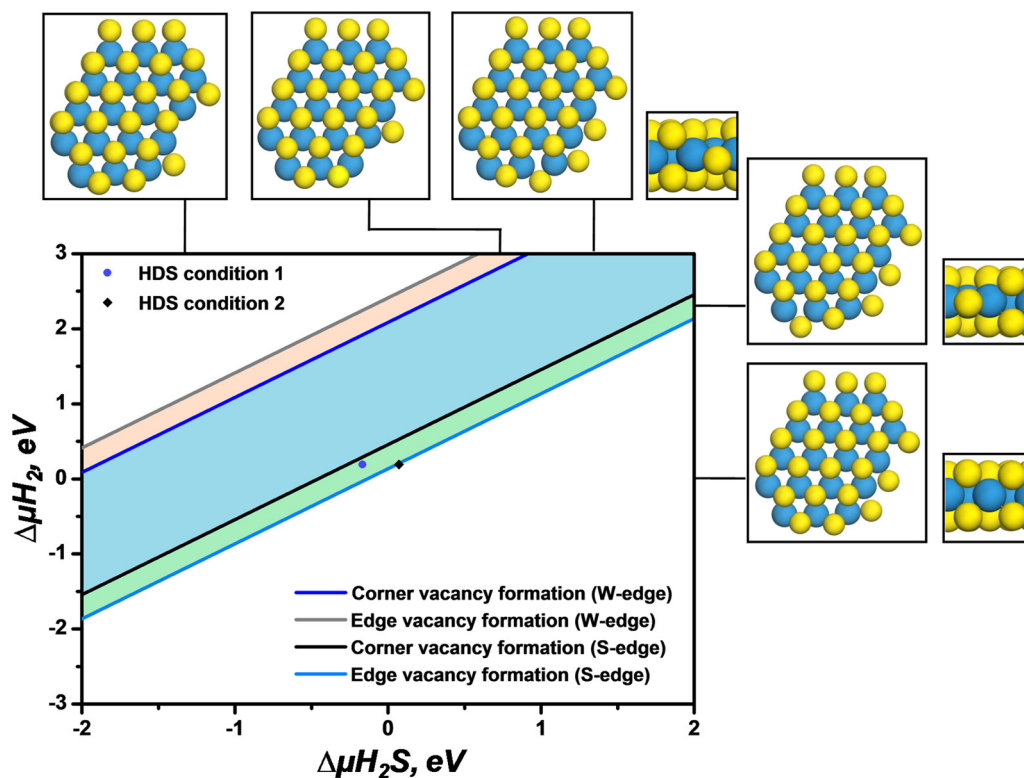
Fig. 7. Phase diagram for single sulfur vacancy formation over different sites of WS$_2$ active phase.

the corner or edge sites (S-edge Fig. S7), double sulfur vacancies are more difficult to be formed at the W-edge (Fig. S8).

3.2.2. NiWS active phases

Subsequently, the formation of sulfur vacancies at different sites of NiWS active phase is studied. The position of Ni is the same as that of MoS$_2$ active phase. Firstly, the formation of one Corner vacancy over the NiWS-I active phase is investigated in Fig. S9(A). It can be seen that the HDS condition 1 is close to the phase region, which is similar to that of NiMoS-I active phase. And it is clear that the reaction condition can be located in the phase region when the H$_2$S partial pressure is very low. Therefore, the formation of one Corner vacancy at the S-edge over NiWS-I is similar to that over NiMoS-I. From Table S9, it can be seen that the formation of a single sulfur vacancy at the S-edge of NiWS-I is favorable at the initial stage of reaction with $p(H_2S)/p(H_2) = 10^{-5}$. The increase of H$_2$S partial pressure makes the formation of single sulfur vacancy more difficult, therefore, requiring more stringent HDS reaction conditions to realize it.

Fig. S9(B) is the phase diagram of one Edge vacancy formation over the NiWS-I active phase. Similar to the NiMoS-I active phase, the HDS conditions 1 and 2 are also not in the phase region. Compared with Fig. S9(A), it can be found that the HDS conditions 1 is closer to the phase region in Fig. S9(A), meaning that the sulfur vacancy is more inclined to form at the corner site. In addition, it can be found that the formation of the single sulfur vacancy becomes more difficult after the W-edge promoted by Ni atoms, which is similar to that over NiMoS-I active phase. However, based on the phase diagrams (Fig. S9), high reaction temperature and low H$_2$S partial pressure are considered necessary to promote the formation of the single sulfur vacancy at the S-edge of NiWS-I active phase.

Fig. S10 displays the phase diagram of double sulfur vacancies formation over the NiWS-I active phase. It can be seen that under the HDS conditions, the formation of double sulfur vacancies at the corner site is more difficult than those at the edge site, which is consistent with the results over NiMoS-I active phase. Furthermore, compared with

NiMoS-I active phase (Fig. S4), the difference is that the HDS condition 1 is farther from the phase region over the NiWS-I active phase (Fig. S10), which means that the formation of double sulfur vacancies is more difficult at the S-edge of NiWS-I active phase.

Fig. 8 shows the formation of a single sulfur vacancy over the NiWS-II active phase of which the S-edge is further replaced by Ni atoms. As can be seen from Fig. 8, the phase regions of the single sulfur vacancy formed at corner site and edge site are very close, meaning that the difficulty of the sulfur vacancy generated at both sites are very similar, however, the sulfur vacancy at the edge site will be generated preferentially. Compared with the NiWS-I active phase (Fig. S9), the HDS condition 1 (Fig. 8) is in the phase region. However, compared with NiMoS-II active phase (Fig. 4), the HDS condition 2 (Fig. 8) is not in the phase region. Therefore, it is considered that under the high H$_2$S partial pressure, the formation of one single sulfur vacancies over the NiMoS-II active phase (Fig. 4) is easier than that over the NiWS-II active phase.

Table S10 gives the ΔG (550 K ~ 650 K) of one Edge vacancy (S-edge) formation over NiWS-II active phase. It can be seen that when the temperature is 600 K and $p(H_2S)/p(H_2) = 0.1$, $\Delta G = 14.73$ kJ/mol, when the temperature is 600 K and $p(H_2S)/p(H_2) = 0.001$, $\Delta G = -8.24$ kJ/mol, which is less than 0. Therefore, it can be concluded that the H$_2$S partial pressure has a great influence on the formation of sulfur vacancy at the edge site over the NiWS-II active phase, while such sulfur vacancy can be formed under both high and low H$_2$S partial pressures over the NiMoS-II active phase.

The formation of double sulfur vacancies is further investigated over the active phase of NiWS-II, as shown in Fig. 9. Obviously, it is difficult to further generate double sulfur vacancies based on the existence of one Corner vacancy (S-edge) or one Edge vacancy (S-edge). Combing with the results in Fig. 5, double sulfur vacancies can be formed based the existence of one Corner vacancy (S-edge) over the NiMoS-II active phase. Therefore, the formation of double sulfur vacancies over the NiWS-II active phase is relatively difficult, which is different from the NiMoS-II active phase.
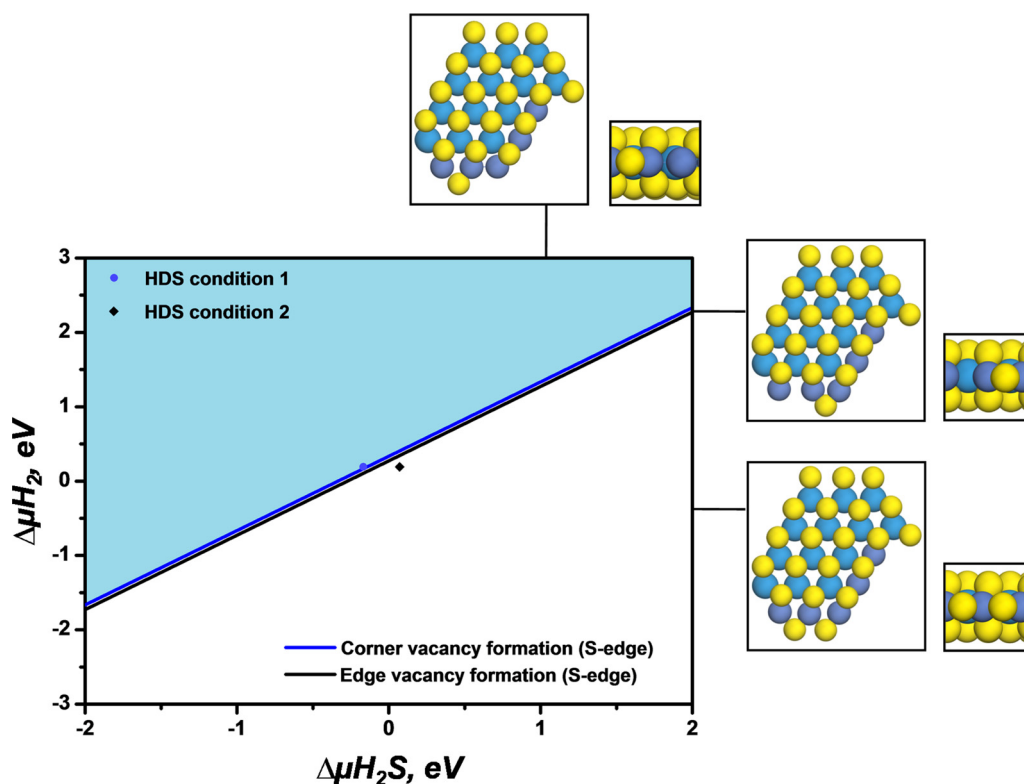
Fig. 8. Phase diagram for single sulfur vacancy formation over the Corner or S-edge of NiWS-II active phase.

3.2.3. CoWS active phases

In this part of the researches, the formation of sulfur vacancies over the CoWS active phase is studied. From Fig. 10, it can be concluded that the difficulty of sulfur vacancy formation over the CoWS active phase follows the order (from easy to hard): Corner vacancy (W-edge) < Corner vacancy (S-edge) < Edge vacancy (S-edge) < Edge vacancy (W-edge). The W-edge is more conducive to the formation of a single sulfur vacancy at the corner site, which is consistent with CoMoS active phase in Fig. 6. Correspondingly, it can be found that the Gibbs free energy variation of one Corner vacancy (W-edge) formation is -26.61 kJ/mol at 600 K and $p(H_2S)/p(H_2) = 10^{-5}$ from the data in Table S11. Overall, the sulfur vacancies over the CoWS active phase are easier to be formed at the corner site rather than at the edge site. In addition, it can be seen that the phase regions of the Edge vacancy (S-edge) and Corner vacancy (S-edge) are very close (Fig. 10), which is similar to the single vacancy formation over the NiWS-II active phase (Fig. 8). Moreover, it can be found that the Edge vacancy (W-edge) is still the most difficult to be

generated. However, according to the calculation results, only the HDS condition 1 is located in the phase region of Corner vacancy formation (W-edge). Therefore, it is believed that only one sulfur vacancy can be formed at the corner site of W-edge of CoWS active phase under the traditional HDS reaction conditions.

And then on the basis of one sulfur vacancy existing at the corner site of W-edge, the formation of double sulfur vacancies is further calculated, as shown in Fig. S11. Unlike the CoMoS active phase, there are obvious differences between the formations of double sulfur vacancies at the edge and corner sites over the CoWS active phase, while the phase regions of forming these double sulfur vacancies are closer over the CoMoS active phase. At the same time, the HDS condition 1 and 2 are not located in the phase region, which is also consistent with CoMoS active phase. Therefore, it can be found that the formation of double sulfur vacancies at the corner site is relatively difficult for CoWS active phase.

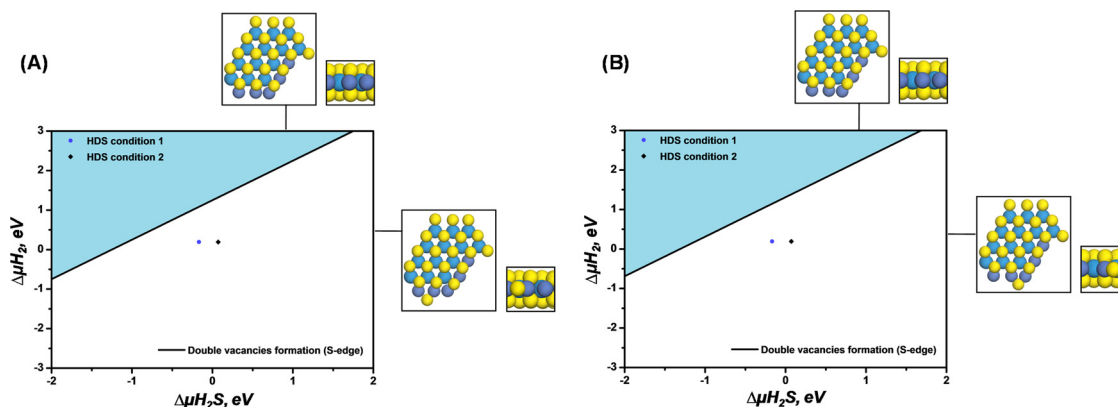Furthermore, the formations of double sulfur vacancies are

Fig. 9. Phase diagrams for double sulfur vacancies formation over the S-edge of NiWS-II active phase: (A) from single vacancy at the Corner; (B) from single vacancy at the S-edge.
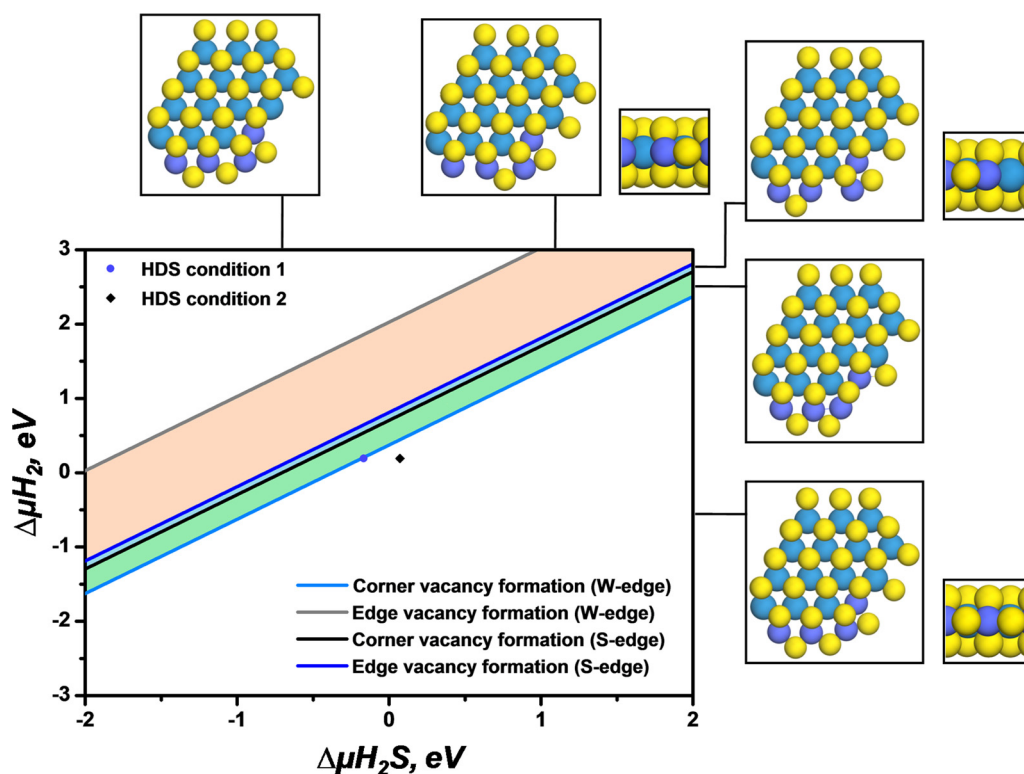
Fig. 10. Phase diagram for single sulfur vacancy formation over different sites of CoWS active phase.

investigated at the S-edge, and the calculation results are shown in Fig. S12. It can be seen from Fig. S12(A) that the removal of one sulfur atom from the adjacent W atom cannot take place under the HDS conditions 1 and 2 based on the existence of one Corner vacancy (S-edge), which is unlike CoMoS active phase. Subsequently, based on the existence of one Edge vacancy (S-edge), the generation of double sulfur vacancies is further investigated in Fig. S12(B). It can be seen that the HDS conditions 1 and 2 are also not located in the phase regions. Based on the calculations of double sulfur vacancies formation at different sites of CoWS active phase, it is found that the formation of double sulfur vacancies over the CoWS active phase is difficult. Compared with the CoMoS active phase, either the single sulfur vacancy or double sulfur vacancies is difficult to be generated over the CoWS active phase.

3.3. Comparison between unpromoted MoS_2 and promoted MoS_2 active phases

Based on the previous calculation results, the Gibbs free energy changes (ΔG) in the formation of the single and double sulfur vacancies over different active phases are summarized in Table 1 and Table 2. From Table 1, it can be found that the edge ($\Delta G = $ -12.74 kJ/mol) and corner ($\Delta G = $ -74.82 kJ/mol) sites of S-edge over MoS_2 active phase and is more favorable to form sulfur vacancies than the M-edge ($\Delta G = 151.92$ kJ/mol and 142.89 kJ/mol for the edge and corner sites, respectively). Under the traditional HDS reaction conditions of 600 K, $p(H_2) = 4$ MPa and $p(H_2S)/p(H_2)/ = 0.001$, the single sulfur vacancies will be easily formed at edge and corner sites of S-edge. Moreover, increasing the reaction temperature and H_2 pressure or decreasing the H_2S partial pressure will be beneficial to the sulfur vacancy formation. However, it will be very difficult to form double sulfur vacancies at edge and corner sites of the MoS_2 active phase.

When Ni covers the M-edge of MoS_2 active phase, the rule of Corner vacancy (S-edge) < Edge vacancy (S-edge) is also observed. However, compared with MoS_2 active phase, the formation of one Corner vacancy (S-edge) over the NiMoS-I active phase becomes difficult (ΔG

Table 1

Gibbs free energy change (ΔG) in the formation of a single sulfur vacancy over different active phases.

Active phases	ΔG (kJ/mol)			
	Edge site (Sulfur-edge)	Corner site (Sulfur-edge)	Edge site (Metal-edge)	Corner site (Metal-edge)
MoS_2	−12.74	−74.82	151.92	142.89
NiMoS-I	41.23	8.50	–	–
NiMoS-II	−77.32	8.10	–	–
CoMoS	−16.48	122.18	31.41	−22.89
WS_2	−21.46	9.62	198.32	166.69
NiWS-I	25.91	0.65	–	–
NiWS-II	−8.24	−2.35	–	–
CoWS	43.74	33.40	161.04	1.48

ΔG is calculated under the conditions of 600 K, $p(H_2) = 4$ MPa, $p(H_2S)/p(H_2) = 0.001$.

Table 2

Gibbs free energy change (ΔG) in the formation of double sulfur vacancies over different active phases.

Active phases	ΔG (kJ/mol)		
	Edge site (Sulfur-edge)	Corner site	Edge site (Metal-edge)
MoS_2	45.51	106.67	192.11
NiMoS-I	7.81	–	–
NiMoS-II	−28.90	–	–
CoMoS	66.47	57.31	26.62
WS_2	−13.89	150.49	254.65
NiWS-I	32.42	–	–
NiWS-II	86.17	–	–
CoWS	112.86	56.10	105.32

ΔG is calculated under the conditions of 600 K, $p(H_2) = 4$ MPa, $p(H_2S)/p(H_2) = 0.001$.

= 8.50 kJ/mol), during which more stringent reaction conditions are needed to realize the Corner vacancy formation (Fig. S3). In addition, based on the existence of a single Corner vacancy at the S-edge of NiMoS-I, the HDS condition 1 (600 K, $p(H_2) = 4$ MPa and $p(H_2S)/p(H_2) = 0.001$) is very close to the phase region, and double sulfur vacancies can be formed at low H_2S pressure which is different from the MoS_2 active phases. As Ni further replaces Mo atoms of S-edge (NiMoS-II), the formation of Edge vacancy (S-edge) becomes easier ($\Delta G = -77.32$ kJ/mol), and the HDS condition 1 with low H_2S partial pressure is very close to the phase region of the Corner vacancy (S-edge) formation. From Table 2, it can be found that the S-edge of NiMoS-II active phase is favorable to generate double sulfur vacancies ($\Delta G = -28.90$ kJ/mol) based on the existence of Corner vacancy (S-edge).

When Co covers the S-edge of MoS_2 active phase, the formation of single sulfur vacancy is arranged according to the following orders (from easy to hard): Corner vacancy (M-edge) < Edge vacancy (S-edge) < Edge vacancy (M-edge) < Corner vacancy (S-edge). That is, the M-edge of CoMoS active phase is more conducive to the formation of the single sulfur vacancy at the corner site ($\Delta G = -22.89$ kJ/mol), meaning that the formation of sulfur vacancy becomes easier at the corner site of M-edge when the Mo atom of this site is substituted by Co atom. In addition, it can be found that with the promotions of Co and Ni atoms, the formation of single sulfur vacancy at the S-edge will become more favorable. Based on the calculation results of the double sulfur vacancies formation over the CoMoS active phase (Table 2), it is found that it is relatively difficult to generate double sulfur vacancies at the corner or edge sites of the CoMoS active phase under the HDS condition 1. Therefore, unlike the NiMoS active phase, the occurrence frequency of double sulfur vacancies over the CoMoS active phase will be very low.

3.4. Comparison between Mo-based and W-based active phases

By calculating the formation of sulfur vacancies over the W-based active phases, it can be found that the difficulty of sulfur vacancy formation over the WS_2 active phase follows the order (from easy to hard): Edge vacancy (S-edge) < Corner vacancy (S-edge) < Corner vacancy (W-edge) < Edge vacancy (W-edge). Based on the results, the S-edge is more advantageous to the formation of single sulfur vacancy than the W-edge of WS_2 active phase, which is consistent with the results of MoS_2 active phase. And under the traditional HDS reaction conditions, it is difficult to form sulfur vacancies at the metal edges over the WS_2 active phase and MoS_2 active phase. Furthermore, it can be seen from Table 2 that under the HDS conditions of 600 K, $p(H_2) = 4$ MPa and $p(H_2S)/p(H_2) = 0.001$, double sulfur vacancies cannot be formed at the corner sites of WS_2 active phase and MoS_2 active phase due to the positive ΔG values of 150.49 kJ/mol and 106.67 kJ/mol. Therefore, it can be seen that for MoS_2 and WS_2 active phases without the promotion of Ni or Co, the formation of double sulfur vacancies at the corner site will be very difficult.

For NiWS and NiMoS active phases, it can be found that when Ni atoms only replace metal atoms of the metal edges (W-edge/Mo-edge), the formation of sulfur vacancies over the NiWS active phase is similar to that over the NiMoS active phase. When H_2S partial pressure is low (at the initial stage of reaction), the formation of one Corner vacancy (S-edge) is favorable. However, with the increase of H_2S partial pressure, the formation of such vacancy at the S-edge will become more difficult. In addition, with the promotion of Ni atoms occurring at the S-edge, it can be found that the sulfur vacancies over the NiMoS active phase can be generated even at high H_2S partial pressure. However, the formation of sulfur vacancies over the NiWS active phase is only possible under the low H_2S partial pressure (Fig. 8). Besides, it is worth noting that the formation of double sulfur vacancies over the NiWS active phase is very difficult ($\Delta G = 86.17$ kJ/mol), while it is relatively easier over the NiMoS active phase ($\Delta G = -28.90$ kJ/mol).

Comparing the formations of sulfur vacancies over CoWS and

CoMoS active phases, it can be found that the W-edge of CoWS active phase is more conducive to form one single sulfur vacancy, which is the similar to CoMoS active phase. However, under the traditional HDS conditions, the single sulfur vacancy can be generated at the edge site of S-edge over the CoMoS active phase ($\Delta G = -16.48$ kJ/mol), while it is comparably difficult to form this vacancy over the CoWS active phase ($\Delta G = 43.74$ kJ/mol). Further comparison of the ΔG values confirms that the formation of double sulfur vacancies over the corner sites of CoMoS and CoWS are difficult ($\Delta G = 57.31$ kJ/mol and 56.10 kJ/mol, respectively). Thus, the frequency of double sulfur vacancies over Co-promoted active phase will be very low. Only there is existing one Corner vacancy (S-edge), the formation of double sulfur vacancies is possible over the CoMoS active phase.

3.5. Comparison with the previous theoretical results

The role of corner sites, especially the corner vacancy in the HDS mechanism of sterically hindered sulfur-containing molecule has been attracted extensive attentions [33,34]. Based on the previous DFT researches, Grønborg et al. [26] reported that the formation of a single sulfur vacancy at the corner site of M-edge over CoMoS active phase is favorable under the HDS condition. Compared with the results of our research, the formation of such vacancy is also preferred over a similar CoMoS model, of which the M-edge is also partially substituted by Co atoms. In addition, Šarić et al. [24] studied the adsorption of DBT molecule over different active sites of CoMoS including the corner site of M-edge, which provided a strong chemical adsorption site for the S-containing compounds and a highly active site for the C−S bond scissions, and our results strongly support this result. It is found that the terminal corner site is necessary which can expose highly accessible active sites, allowing for the adsorption of sterically hindered sulfur-containing molecule.

Based on the previous researches on the adsorption of sulfur-containing compounds [24], it can be found that only one single corner vacancy is not sufficient for the 4,6-DMDBT adsorption in σ-mode. However, it can be found that the formations of double sulfur vacancies over MoS_2 and CoMoS active phases are relatively difficult under the HDS conditions in this research. In addition, double sulfur vacancies are also hard to be generated over the W-based active phases. Therefore, the amounts of double sulfur vacancies will be present at a very low frequency over the terminal corner site, which explains the low direct desulfurization activity of 4,6-DMDBT. Nevertheless, it is interesting that when Ni atoms continue to replace Mo atoms at the S-edge of the NiMoS active phase, the formations of double sulfur vacancies become more favorable, which can expose more accessible Ni sites for adsorptions of the sulfur-containing molecules. This research provides a deep insight into the structure of active phase under the HDS conditions, which can be used to design the highly active HDS catalyst toward the most refractory sulfur molecules.

4. Conclusions

In this research, DFT calculations are employed to investigate the formation of sulfur vacancies over different active sites of Mo-based and W-based active phases under the traditional HDS reaction conditions, which promote the understanding of the active phase structures from the atomiC–Scale. And the main conclusions are summarized as follows:

(1) Under the traditional HDS reaction condition (600 K, $p(H_2) = 4$ MPa and $p(H_2S)/p(H_2) = 0.001$), the single sulfur vacancy will be easily formed at the sulfur edges than that at the metal edges (M-edge/W-edge) over both unpromoted MoS_2 and WS_2 active phases.

(2) When Ni atoms only replace metal atoms of the metal edges (M-edge/W-edge), a single sulfur vacancy at the corner site of the S-edge is easier to form at low H_2S partial pressure (considering at the initial stage of reaction), but with the increase of H_2S partial pressure, the formation of such vacancy at the S-edge will become more difficult.

(3) When the S-edges of the MoS$_2$ active phases are promoted by Co and Ni atoms, the formation of a single sulfur vacancy (one CUS site) at the S-edge will become more favorable. Similar rules can be observed over the active sites of Co or Ni-promoted WS$_2$ active phases, but the generation processes are more difficult than those over the promoted MoS$_2$ active phase.

(4) The formation of double sulfur vacancies will be difficult under the HDS conditions over most transition metal active phases in our researches. However, it is interesting that when Ni atoms continue to replace Mo atoms at the S-edge of the NiMoS active phase, the formations of double sulfur vacancies become more favorable, which can expose more accessible Ni sites for molecule adsorptions.

(5) The temperature and pressure are two important factors affecting the sulfur vacancy formation. And it will be beneficial for the formation of the sulfur vacancy through increasing the reaction temperature, H$_2$ pressure and decreasing the H$_2$S partial pressure.

Declarations of interest

None.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcatb.2019.117937.

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